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RATES OF BASIC ION-MOLECULAR PROCESSES IN THE IONOSPHERE

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SUMMARY

The rate of basic ion-molecular processes are discussed on the basis of the review of twenty-nine works by various authors and the comparison of laboratory experiments with theoretical considerations.

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The determination of constants of the rate of ionization recombination processes in the upper atmosphere is beset with well known difficulties. As follows from the review paper [1] , the span of laboratory investigations of the basic reaction constants is very broad and it does not allow to pinpoint reliable values for the investigation of ion-molecular reactions in the ionosphere and in the laboratory, which require discussion in order to select the most reliable values of constants.

We compiled in Table 1 the results of laboratory investigations of two basic ionospheric ion-molecular reactions

$$O^+ + N_2 \rightarrow NO + N \quad \gamma_1 \tag{1}$$

$$O^+ + O_2 \rightarrow O_2^+ + O \quad \gamma_2 \tag{2}$$

As may be seen from Table 1, even if we reject the high value of $2 \cdot 10^{-10}$ cm^3 sec^{-1}, brought out by Paulson (inasmuch as it is in contradiction with the estimate [9], $\gamma_1 \leqslant 5 \cdot 10^{-11}$ cm^{3}sec^{-1} brought out in the same author's review paper), and also the high value $\gamma_1 \approx 10^{-8}$ см$^3 \cdot$ sec^{-1}, which,

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TABLE 1

No.	AUTHORS	Constants of reactions (1) and (2) in $cm^3\ sec^{-1}$	
		γ_1	γ_2
1	R. F. Potter [2]	10^{-8}	-
2	R. H. D. Dickinson [3]	—	$2.5 \cdot 10^{-11}$
3	V. L. Talrose et al [4]	$\leqslant 6.7 \cdot 10^{-11}$	
4	[5] G. F. O. Langstroth, J. B. Hast.	$4.7 \cdot 10^{-12}$	$1.8 \cdot 10^{-12}$
5	Fite, et al. [6]	—	$(1\text{–}10) \cdot 10^{-11}$
6	Volpi, et al. [7]	$2.2 \cdot 10^{-11}$	—
7	Sayers, Smith [8]	$2.7 \cdot 10^{-11}$	$1.6 \cdot 10^{-11}$
8	Paulson, Mosher	$\leqslant 5 \cdot 10^{-11}$	—
9	Paulson, et al. [10]	$2 \cdot 10^{-10}$	—
10	Fehsenfeld, et al. [11] [12]	$3 \cdot 10^{-12}$	$4 \cdot 10^{-11}$

as already noted more than once, is probably erroneous, there is observed a scattering of the most reliable among the obtained values of the constant of the reaction's (1) rate by one order of magnitude; at the same time, both the upper and the lower values are corroborated by two experiments. A somewhat better position is observed for the constant of reaction (2); however, here too it is necessary to deny oneself the result of the experiment [5], which as will be seen further, will give a value γ_1 more acceptable from the viewpoint of ionospheric investigations so that the remaining values γ_2 may be matched with a precision to the factor 2.

The estimates of the effectiveness of the same processes (1) and (2), obtained by various authors on the basis of analysis of ionospheric data, are compiled in Table 2. Here it should be noted that different initial data were utilized by the various authors, as for example: the altitude variation of the ion composition in the region 100—200 km [16], the altitude and daily variations of ion concentrations [17], the measurements of the linear recombination coefficient in the F_2-region [19] and so forth. In order to obtain the estimates brought out in the eighth line of Table 2, the relations between ion-molecular reaction and dissociative recombination constants [24—26]

$$\gamma_1 / \alpha^*_{NO^+} = (5\text{—}10) \cdot 10^{-5}, \qquad \gamma_2 / \alpha^*_{O_2^+} = (1\text{—}2) \cdot 10^{-4}$$

were utilized. The quantities $\alpha^*_{NO^+}$ and $\alpha^*_{O_2^+}$, which were more reliably investigated in the laboratory than the constants γ_1 and γ_2, were borrowed from the review paper [2] for a temperature of the order of 1000° K. Therefore, the estimates of γ_1 and γ_2 brought up above, also refer to the indicated temperature.

It may be seen from the data brought out in Table 2 that the ionospheric

TABLE 2

No.	AUTHORS	Constants of Reaction (1) and (2) $cm^3\ sec^{-1}$	
		γ_1	γ_2
1.	Bates, Nicolet [14]	$\gamma_1 + 0.16\ 2 = 1.3 \cdot 10^{-13}$	
2.	Khartek, Rive [15]	$\leqslant 10^{-13}$	$\leqslant 10^{-12}$
3.	Norton, et al [16]	$1 \cdot 10^{-12}$	$5 \cdot 10^{-11}$
4.	Danilov [17]	$(0.5\text{-}1) \cdot 10^{-12}$	$(0.5\text{-}1) \cdot 10^{-11}$
5.	Whitten, Poppoff [18]	$2 \cdot 10^{-12}$	$2 \cdot 10^{-11}$
6.	Nisbet, Quinn [19]	$\leqslant 1.3 \cdot 10^{-12}$	$\leqslant 10^{-11}$
7.	Sagalyn, Smiddy [20]	$(1.6\text{-}3.2) \cdot 10^{-12}$	—
8.	Danilov (γ_1/α^* & α^*)	$(1.5\text{-}3) \cdot 10^{-12}$	$(0.6\text{-}1.1) \cdot 10^{-11}$
9.	Hall, et al [22]	$\gamma_1 + 0.12\,\gamma_2 \approx 3 \cdot 10^{-12}$	
10.	Danilov, Yatsenko [23]	$\gamma_1/\gamma_2 \approx 0.1$	

estimates by the various authors are not generally divergent among themselves, leading to respective mean values of constants of processes (1) and (2)

$$\gamma_1 = 2 \cdot 10^{-12}\ \text{см}^3 \cdot \sec^{-1}$$

$$\gamma_2 = 2 \cdot 10^{-11}\ \text{см}^3 \cdot \sec^{-1}$$

these mean values of γ not differing from the most reliable estimates brought out in the lines 3 to 9 of Table 2 by more than 2—3 times. The values of γ, obtained in [14, 15] should be recognized as underrated. They agree with neither the most reliable ionospheric estimates, nor the laboratory data. As to the latter, the quantities γ_1 and γ_2 obtained from the ionospheric data allow to assert that the quantities γ_1 arrived at in the works [5, 11], are correct whereas those obtained in the experiments [7, 8] are overrated.

It should be analogously admitted that the value

$$\gamma_2 = 1{,}8 \cdot 10^{-12}\ \text{см}^3\ \sec^{-1}$$

is strongly underrated, while that obtained in recent experiments

$$\gamma_2 = 4 \cdot 10^{-11}\ \text{см}^3 \cdot \sec^{-1}$$

is somewhat overrated.

The obtained estimates of constants of basic ion-molecular reactions in the ionosphere appear to be sufficiently reliable (in any case, within the limits of a factor of 2). Some uncertainty is introduced only by the temperature dependence of constants γ_1 and γ_2. According to the experiments of the work [8], the reaction's (2) constant depends on the temperature in the form T^{-1} in the region $210^\circ \leqslant T' \leqslant 452^\circ$ K. From theoretical considerations, it appears that generally the ion-molecular reaction constants' dependence on temperature must not be observed [9, 27, 28]. According to [13] a direct dependence between γ_1 and T was obtained in the experiments at energies of several ev. The question of the constants' temperature dependence thus requires further experimental research.

TABLE 3

Reactions	Fite [6] et al	Volpi[7] et al	Paulson & al [10]	Ferguson [11-13] & al	Harteck [29]
$N^+ + O_2 \rightarrow NO^+ + O$ (3)	$5 \cdot 10^{-10}$	$1 \cdot 10^{-10}$	$3 \cdot 10^{-10}$	$5 \cdot 10^{-10}$	10^{-10}
$O_2^+ + N_2 \rightarrow NO^+ + NO$ (4)	—	$\leqslant 2 \cdot 10^{-18}$	$4 \cdot 10^{-11}$	$< 10^{-15}$	—
$N_2^+ + O_2 \rightarrow NO^+ + NO$ (5)	$2{,}1 \cdot 10^{-13}$	$\leqslant 2 \cdot 10^{-18}$	$4 \cdot 10^{-11}$	—	—
$N_2^+ + O_2 \rightarrow O_2^+ + N_2$ (6)	$2 \cdot 10^{-10}$	—	—	$1{,}0 \cdot 10^{-10}$	—
$N_2^+ + O \rightarrow NO^+ + N$ (7)	—	—	—	$2{,}5 \cdot 10^{-10}$	—
$N_2^+ + O \rightarrow N_2 + O^+$(8)	—	—	—	$< 10^{-11}$	—
$N^+ + O_2 \rightarrow O_2^+ + N$ (9)	—	—	—	$(0{,}5—1) \cdot 10^{-9}$	—

Compiled in Table are the results of laboratory measurements of constants of ion-molecular reactions in which the main components of the atmosphere O , O_2 and N_2 take part. The bulk of these reactions was investigated in the works [11 – 13]. As in Table 1, attention is drawn here by the values obtained by Paulson, sharply diverging from the data by other authors, which compels us to assume that the Paulson experiment [10] is erroneous. The ionospheric estimates of these reactions' constants are more complex than those of the basic reactions (1) and (2). Particular attention should be given the values

$$\gamma_7 \approx 1{,}0 \cdot 10^{-11}\ \text{cm}^3\ \text{sec}^{-1}$$

obtained in [16]

$$\gamma_7 \approx 2 \cdot 10^{-11}\ \text{см}^3\ \text{sec}^{-1}$$

obtained in [18] , and also

$$\gamma_4 = (3—10) \cdot 10^{-14}\ \text{см}^3\ \text{sec}^{-1}$$

made in the work [26] on the basis of analysis of data on the ion composition of the region 100—150 km.

The results of laboratory experiments on the constants of ion-molecular processes with the participation of small atmospheric admixtures, such as the neutral molecules NO and nitrogen atoms, are compiled in Table 4

TABLE 4

Reactions	Value of γ according to [13]
$O^+ + NO \rightarrow NO^+ + O$ (10)	$(2{,}4 \pm 1) \cdot 10^{-11}$
$N_2^+ + NO \rightarrow NO^+ + N_2$ (11)	$5 \cdot 10^{-10}$
$O_2^+ + NO \rightarrow NO^+ + O_2$ (12)	$8 \cdot 10^{-10}$
$O_2^+ + N \rightarrow NO^+ + O$ (13)	$(1{,}8 \pm 0{,}5) \cdot 10^{-10}$
$N^+ + NO \rightarrow NO^+ + N$ (14)	$(8 \pm 1) \cdot 10^{-10}$

As may be seen, the values of constants obtained in the laboratory are very high. Therefore, the opinion having prevailed to-date that the indicated reactions may be disregarded on account of low concentrations of NO and N must be revised. The exact values of the indicated concentrations are so far unknown; however, the high values of constants require detailed analysis

of these processes when considering the equilibrium concentrations of ions, particularly in the region 100—130 km.

* * * THE END * * *

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